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(54) Title: PROCESS FOR THE REMOVAL OF PHOSPHOROUS (57) Abstract A process for the removal of phosphorous, in the form of orthophosphate, from an aqueous stream comprising the introduction into the stream of an effective amount of calcium ions, preferably gypsum derived, adjusting the pH to between about 5 and 8, introducing the stream into a reaction vessel wherein it is brought into contact with a gently stirred bed of fine particulate magnesia in an amount sufficient to fix the so-formed calcium phosphate, the pH of the stream in contact with the magnesia being from about 8 to 12 and removing a stream from the vessel which is depleted in phosphorous.		

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- 1 -

PROCESS FOR THE REMOVAL OF PHOSPHOROUSField of the Invention

This invention relates to processes for removal of phosphorous from aqueous streams, and in particular to a process whereby the phosphorous is present as orthophosphate and is removed by adsorption onto hydrated magnesium oxide in the form of calcium salts.

Background to the Invention

The presence of phosphorous in aqueous streams which enter the environment has been recognised as undesirable due to the role of this element in lake and river eutrophication. Although appreciable amounts of phosphorous may enter water courses through groundwater which has leached phosphorous from the surrounding soils (particularly in agricultural areas fertilised with phosphorous containing chemicals), significant quantities of phosphorous enter the aquatic environment from sewage and industrial effluent streams. In the Hawkesbury/Nepean River system near Sydney Australia for example, it has been estimated that from 1/3 to 1/2 of the ambient dissolved phosphorous originates from sewage.

The problems of excessive phosphorous in water courses has been recognised for some time, and the prior art is replete with methods which seek to address the problem. The aim of these processes has been to produce an aqueous effluent sufficiently depleted in phosphorous such that its quality complies with relevant environmental legislation.

One general approach to phosphorous removal has been to treat the phosphorous containing stream with metal salts, thus forming an insoluble metal phosphorous which is removed from the stream through sedimentation or other means. Some examples of this method include the use of aluminium or ferric salts, and also of lime. In this process insoluble phosphates of aluminium, iron or

- 2 -

calcium are formed.

While these methods have proved reasonably successful in meeting existing regulatory standards, as environmental requirements on the phosphorous effluent streams become
5 more stringent, it is unlikely that they will perform to the revised standards without significantly increasing the dose rates, and/or very substantial engineering upgrade of existing sewage treatment plants. An indication of the measures required to consistently lower sewage effluent
10 phosphorous levels to 0.15mg/L using iron salts can be gained from the paper of D M Philp J. Wat. Poll. Cont. Fed. 57(8) 1984, pp 841-846 which describes phosphorous removal at a large sewage works near Canberra, Australia.

Plant upgrades to utilise metal salts will entail
15 modest capital costs as well as increased operating costs, but more importantly, the use of these chemicals for phosphorous precipitation produces very gelatinous sludge products which are difficult to handle and to de-water. Typically the use of chemical precipitation to remove
20 phosphorous from sewage streams increases sludge volume by 30-40%, and this entails increased transport and landfill disposal costs concomitant with the increased sludge volume. The sludge will also contain increased amounts of aluminium or iron which may detract from its application
25 as a fertiliser supplement for agriculture. Again the use of these chemicals can, in some cases, compromise the performance of various biological treatments designed to remove carbon and nitrogen, since they may affect the operating pH of the bioreactors.

30 A further consideration is that considerable tonnages of potentially valuable phosphorous are lost to the sludge. For example, it is estimated that a city with population 500,000 loses around 300 tonnes (of elemental phosphorous) per annum to its sewage sludge through the
35 use of chemical precipitation.

- 3 -

The other general approach to phosphorous removal constitutes the use of adsorbants. In this approach phosphorous is caused to precipitate in either an amorphous or crystalline form onto a suitable medium
5 whereby it remains adsorbed thereon. Once the medium has become sufficiently loaded with phosphorous, it is removed and either employed further to recover the phosphorous and regenerate the medium, or may be employed directly as a source of phosphorous in, for example, certain fertiliser
10 formulations. To the extent that this approach results in a small volume of product loaded with recoverable and reusable phosphorous, it would appear superior to other methods. Moreover, overall sludge volumes from the treatment of sewage are reduced.

15 The absorption approach has been recognised in the prior art as being useful for the removal of phosphorous from aqueous streams. In Pac. Chem. Eng. Cong. 4, 259-264 (1983), Hirasawa et al describe a process for phosphorous removal whereby phosphorous is removed as crystalline
20 hydroxyapatite which forms on a medium such as phosphorous rock or bone char. These media are said to induce the crystallisation. In this process, a phosphorous containing effluent stream is first decarbonated and then an appropriate amount of calcium hydroxide is added.
25 Thereafter in one form the treated stream is passed through a sand filter and then through a fixed bed of media. Treated water flows out of the fixed bed. In another form, the treated stream is passed through a fluidised bed of media, then through a sand filter and
30 finally through a fixed bed of media. Treated water flows out of the fixed bed.

The authors report that at $100\text{m}^3/\text{day}$ a secondary sewage effluent containing 2-3mg/L of phosphorous was reduced to 0.26-0.35mg/L of phosphorous.

- 4 -

In J. Water Pollut. Cont. Fed. 60(7), 1239-1244 (1988), Kaneko et al describe a process for phosphorous removal using a granular activated magnesia clinker said to have a composition of 95% MgO, 3% CaO and 1% SiO₂.
5 Essentially the process comprises addition of sodium hydroxide and calcium sulphate to a secondary sewage effluent to adjust the pH to 8-9 and calcium concentration to 50-60mg/L. The treated solution is passed downwardly through a sand filter to removed suspended solids and then
10 through a column containing the granular activated magnesia clinker to remove the phosphorous. At a flow rate of 3.0m³/m³ MgO bed volume/hour, phosphorous was removed (as phosphorous) from 2-5mg/L to levels less than 0.5mg/L. When effluent phosphorous levels exceeded this
15 level, after around 8 months of operation, the magnesia was regenerated using 2% acetic acid. The authors reported that decarbonation of the influent was not necessary.

Some related Japanese developments appear to rest on
20 the foundations of the work discussed above. Thus in Japanese patent application 1216795-A, it is disclosed that phosphorous is removed from effluent streams in a fluidised bed system containing various phosphorous absorbing materials including "lightly burned magnesia".
25 The process as described in this patent application involves significant recycle of the phosphorous depleted effluent stream - presumably as an aid to the fluidisation of the reaction bed - and also appears to require the addition of anionic polymer to the reacting mass.

30 In Wat. Res. 25(8), 959-965(1991), Roques et al describe another process for phosphorous removal from sewage, in this case using a half burnt dolomite as the phosphorous fixation medium. These authors report that the media consisted of a equimolar mixture of MgO and
35 CaCO₃ and was 0.5-2.0mm in diameter with a mean diameter

- 5 -

of 1.5mm. Experiments showed that the 0.5mm grains had a phosphorous absorbing capacity of 10mg PO_4 /gram of medium. Acid regeneration of the medium was unsuccessful due to excessive dissolution of the media itself. Since
5 it was found that phosphorous fixation capacity was related to the specific surface area of the media, a pulverised material with specific surface area of $1200\text{m}^2/\text{m}^3$ - as opposed to the $3900\text{m}^2/\text{m}^3$ of the "standard" material - was tested. Use of this material
10 doubled the phosphorous loading capacity to around 20mg PO_4 /gram of medium. The authors note in their conclusion that finely pulverised medium (mean diameter <100 micron) "should be introduced into a poor axial mixed tank in order that the material incorporates
15 directly into the bacterial floc. This will aid retention of the solids during its passage in the sedimentation tank. The quantity of sludge produced would not increase excessively and the post pH value would permit direct discharge of the treated effluent into the natural
20 environment."

It appears that these authors see a role for this process as an aid to final settling of the floc produced during biological treatment, with the added benefit of also removing some phosphorous.

25 Disclosure of the Invention

The present inventions, whilst recognising the utility of the prior art crystallisation/absorption processes for phosphorous removal, have surprisingly found that by using a magnesia of relatively fine particle size
30 in a gently stirred bed, a highly efficient process for phosphorous removal from an aqueous stream is achieved.

Accordingly, the present invention consists in a process for the removal of phosphorous, in the form of orthophosphate, from an aqueous stream, comprising
35 introducing into the stream an effective amount of calcium

- 6 -

ions, optionally decarbonating the stream, adjusting the pH to between about 5.0-8.0, introducing the stream into a reaction vessel, contacting the stream with an amount of magnesium oxide in the form of fine particles sufficient to fix the so-formed calcium phosphate, whilst agitating the magnesium oxide and removing a stream from the vessel which is depleted in phosphorous.

Using the process of this invention, orthophosphate levels may typically, and reliably be reduced from several hundred mg/L (as phosphorous) in the influent stream to 0.3mg/L (as phosphorous) or less in the effluent in a continuous manner. Moreover, the final solid product from the reactor is significantly enriched in phosphorous and - depending on how the process is operated - may contain from between 5-18% or greater of elemental phosphorous. This represents a premium high grade source of this element suitable for recycling back into various industries.

The aqueous phosphorous containing stream may originate from a number of sources including primary, secondary or tertiary treated sewage effluent and industrial waste or process streams. Such streams may also contain heavy metals which would be detrimental to the environment were they not removed prior to release of the final effluent. However, the basic nature of the magnesia will act to absorb these metals as hydroxide precipitates in addition to its ability in removing phosphorous. For those streams containing an excessive quantity of organic or insoluble particulate matter, it may be necessary to subject the stream to aerobic or anaerobic treatment, possibly followed by sand filtration to remove particulate matter.

Although a wide variety of calcium salts may be used to supplement the stream with calcium, two readily available sources are gypsum - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - and

- 7 -

calcium chloride. The degree to which calcium should be added to the stream depends on the desired phosphorous level in the final effluent, and typically to reduce phosphorous levels from an influent level of P_{in} mg/L to
5 ≤ 0.2 mg/L in the effluent, the calcium in the influent should be \geq or $= [2 \times P_{in} + 80]$ mg/L provided the operating pH of the reactor exceeds 9.7.

A convenient manner in which to augment the influent stream with calcium to the required level is simply to
10 divert a portion of the stream (typically 10-20% of the total flow) to a small stirred tank into which solid gypsum is added at an appropriate rate. This portion of the stream, now substantially saturated with calcium sulphate, is then recombined with the major portion of the
15 influent. If a more soluble calcium salt such as $CaCl_2$ is to be used as the calcium source, then no partial diversion is necessary and a concentrated solution of this salt may simply be bled into the influent stream at an appropriate rate.

20 In some cases it may be desirable to decarbonate the phosphorous containing stream prior to contacting it with the magnesia. Both bicarbonate and dissolved carbon dioxide may interfere with phosphorous deposition by competing for the available calcium leading to
25 co-deposition of $CaCO_3$ - calcite. One means of decarbonating is by adjusting the pH of the stream to 4-4.5 using dilute mineral acid, followed by air stripping. Dilute sulphuric acid is excellent for this purpose. Following this process, it may be desirable to
30 readjust the stream pH to higher values by judicious addition of dilute sodium hydroxide, ammonia, lime or other suitable base.

The decarbonation step may be performed before or after the calcium addition stage. However, it is
35 preferred that any decarbonation is performed prior to

- 8 -

supplementing the influent with calcium.

Once the stream has been so-treated, it is introduced into a reaction vessel, preferably from a lower portion thereof. A reaction vessel that is cylindrical in shape with a conical bottom has been found to be suitable, as this configuration allows for uniform distribution of the effluent. However, any other reactor geometry and influent distribution system allowing for even distribution of the phosphorous containing influent could be employed. A quantity of fine magnesia previously introduced into the vessel is gently agitated by the upflowing stream, while some horizontal motion of the magnesia bed is produced by a slow speed stirrer. The purpose of this agitation is to prevent channel formation in the bed, which would lead to "short circuiting" of the system and consequently reduce the contact time. As the fluid percolates through the magnesia, phosphorous is deposited on the particles as an amorphous precipitate of calcium phosphate.

The magnesia employed for the reactive bed should be in the form of fine particles so as to maximise the activity of this component. A preferred particle size is about 200 microns, preferably about 100 microns or less. If, however, the particles are too small, some of the bed is lost and carried out of the system with the effluent. It has been found that a commercially available magnesia Enviromag 75 - available from ICI - with mean particle diameter of around 10 micron and a particle size distribution such that 95% of the weight passes through a 75 micron screen is suitable. This material has a specific surface area of 40 metre²/gm, and an analysis: MgO 95-97%; CaO 1.5-2.8%; SiO₂ 0.5-0.8%; Al₂O₃ 0.1%; Fe₂O₃ 0.1%; MnO 0.1%.

It should, however, be noted that the disclosure of the use of this material in no way limits the present

- 9 -

invention to use of this material alone. Magnesium oxides or materials containing a substantial amount of magnesium oxide from other sources, used either in their unhydrated or hydrated forms, and having different particle size
5 distribution and chemical compositions could usefully be employed for the removal of phosphorous from waste or other process streams by the method embodied in this invention.

When the process is operated a high rates of
10 throughput it is possible that some solid material may be carried out of the bed. If the level of suspended solids in the resulting effluent is unacceptable, these may be removed through conventional filtration techniques, possibly in conjunction with the use of flocculation and
15 settling, using anionic polymers to promote flocculation of the fine particles.

As a consequence of the deposition of the phosphorous, it has been found that the volume of the fluidised bed begins to increase continuously, and that
20 the rate of increase of the bed volume varies approximately directly to the flow rate of liquid through the reactor, ie, to the "surface loading" and also directly as the concentration of the phosphorous in the influent stream. After some time, however, the bed volume
25 stabilises and the settling properties of the bed improve dramatically. This "stabilisation" of the bed appears to be related to the degree to which the magnesia is hydrated and becomes converted to magnesium hydroxide. The rise in bed volume, particularly when high phosphorous containing
30 streams are pumped quickly through the reactor, necessitates some care in initial operation of the process until the bed stabilises. It has been found, however, that the process may be operated at surface loadings of 0.5-2.0metre/H with influent streams containing up to
35 90mg/L of phosphorous.

- 10 -

Streams with higher phosphorous loadings may also be treated successfully, but may initially have to be pumped, depending on overall reactor volume, at slower rates.

After passing through the reaction and settling
5 processes, the phosphorous depleted effluent is drawn from the reactor, preferably from an upper portion thereof. Typically overall retention times are from 0.5-2 hours. On this point it is important to note that this retention time is governed by the settling properties of the
10 reactant mass rather than by any inherent sluggishness of the chemical kinetics. Thermodynamic, chemical equilibrium is achieved relatively quickly, and the concentration of soluble orthophosphate in the reactor effluent is given by:

15 Total effluent phosphorous (mg/L) and present as orthophosphate = $0.46 \times (1 + 10^{12.37 - \text{pH}}) / \text{Ca}^{1.5}$
with calcium in the effluent measured in mg/L.

Brief Description of the Drawings

Fig. 1 is a flow diagram showing one embodiment of
20 the process of the invention;

Fig. 2 is a flow diagram showing a second embodiment of the process of the invention;

Fig. 3 is a flow diagram showing a third embodiment of the process of the invention;

25 Fig 4 is a flow diagram showing a fourth embodiment of the process of the invention;

Fig. 5 depicts schematically an embodiment of the process as used for Examples 1 and 2;

30 Fig. 6 depicts schematically a larger scale reactor and associated settling tank, used in Examples 6, 7 and 8;

Fig. 7 is a plot of the performance of the process of Example 1;

Fig. 8 is a plot of the performance of the process of Example 2;

35 Fig. 9 is a plot of the performance of the process of Example 4; and

- 11 -

Fig. 10 is a plot of change in bed volume for Examples 6 and 7.

Modes for Carrying Out the Invention

Although the reactor geometry of Fig. 1 was employed
5 for the majority of the examples to be discussed below,
other geometries and reactor configurations are suitable.
One simple variation constitutes a vertical cylindrical
reaction vessel - fitted with a suitable stirring
impeller - again operated in upflow mode.

10 In these configurations the primary vessel is
functioning both as a containment for the various
important reactions, and as a settler, and consequently
must be operated with the upflow velocity less than the
settling velocity of at least the majority of the
15 contained magnesia/calcium phosphate particles.

In Fig. 1 there is shown one embodiment of the
process of the invention. In this embodiment, a
phosphorous containing stream 10 enters vessel 13.
Sufficient acid 14 is added to the phosphorous containing
20 liquid 12 so as to give a pH of about 4.5. Air 11 is then
bubbled through the liquid 12 to complete decarbonation
thereof.

Once the liquid 12 is decarbonated, it is pumped into
the lower conical end 23 of a reaction vessel 22 by
25 pump 21. A portion of the decarbonated liquid 12 is
diverted by pump 18 into another vessel 16. In this
vessel, gypsum 15 is added with stirring so as to produce
the requisite concentration of calcium in the liquid 17.
This is then bled by line 20 back into line 19 so as to
30 effectively provide a calcium loaded stream into the
reaction vessel 22.

Magnesia 24 is loaded into the reaction vessel 22 to
form a bed to a height 26 which, with agitation by
stirrer 25 in combination with the upward flow provided by
35 pump 21, produces maximum contact between the magnesia bed

- 12 -

and the phosphorous containing liquid stream. It must, however, be noted that the degree of overall agitation is controlled to a minimum consistent with the prevention of channelling.

5 After a period of contact between the liquid stream and the magnesia, the liquid now at a depth 27 is drawn off by line 28 to stirrer vessel 32. In this vessel, anionic polymer 30 is added to flocculate solids in the liquid stream 31 contained therein whilst the liquid is
10 agitated by stirrer 29. Flocculant 33 collects after a time and is removed 35 together with phosphorous loaded magnesia 36 from the reaction vessel 22 to be dewatered into a solid 34 and a liquid stream 37. The solid 34 is removed as a phosphorous enriched product 39 suitable as a
15 fertiliser. The stream 37 is fed back into line 28.

 Once deflocculated in tank 32, the phosphorous-depleted stream 40, passes into tank 41 where carbon dioxide 43 is introduced to give pH of about 7-8 for the liquid 42 contained therein. Once the pH is corrected,
20 the phosphorous-depleted stream is discharged as effluent 44.

 In the embodiment shown in Fig. 2, features like those of Fig. 1 have been like-numbered. The principal difference between this embodiment and that of Fig. 1 is
25 that, instead of introducing gypsum into a portion of the decarbonated stream, a gypsum bed 45 is loaded into the reaction vessel 22 in a lower portion thereof and below the magnesia bed 24.

 When operated in this manner, the influent flows
30 firstly through the layer of gypsum where it becomes enriched in calcium ions prior to it being introduced to the upper bed region where the high pH and surface area provided by the magnesium oxide particles allow deposition of amorphous calcium phosphate. This mixed bed
35 configuration obviates the need to supplement the stream

- 13 -

with calcium prior to introduction to the reactor. When operated in this manner, it has been found that the more dense calcium sulphate layer remains substantially separate from the less dense upper strata containing the magnesium oxide and deposited phosphorous compounds. Since the gypsum is appreciably soluble in water, it may be necessary from time to time to replenish the lower layer with fresh gypsum.

The principal disadvantages of this mode of operation are that, due to the appreciable solubility of calcium sulphate, it is probable that the effluent stream will contain a high concentration of this salt, and this may be detrimental to receiving waters in areas where water salinity is an issue. Secondly, the product eventually extracted from the reactor may, to a degree, be contaminated with some unused gypsum.

Another viable operating configuration is where the influent (supplemented in Ca) is pumped into a continuously stirred reactor, which may be of relatively small dimensions, containing a slurry of magnesia. The total reaction mixture is then allowed to overflow into a conventional settling or thickening apparatus (eg, a conical tank or an inclined plate settler) where, after the solids have settled the clear phosphorous depleted liquor is drawn out of the system. The thickened phosphorous laden slurry is then pumped, either wholly or in part, back to the reaction vessel. As the magnesium oxide reactant is consumed by the process, it is necessary to add small quantities of unused MgO to the reaction mixture.

When operated in this manner, the process consists of separate reaction and settling stages, and in some instances may offer advantages over the "single stage" mode of operation described previously. When operated in this manner it may, in some cases, be appropriate to

- 14 -

employ an in line mixer in place of the reaction vessel.

In Fig. 3, this embodiment is shown schematically, with features like those of the embodiments of Figs. 1 and 2 like-numbered. Specifically, the calcium dosed
5 decarbonated phosphorous containing stream is pumped by pump 21 to reaction vessel 100, which contains a magnesia bed 101. This is continuously agitated by stirrer 102. After a time the loaded magnesia/reaction mixture is allowed to overflow 103 into a conventional settling or
10 thickening apparatus, which in this case is a conical tank 104. After the solid 106 settles out, the clear phosphorous depleted liquid is drawn 107 into a tank 32 for deflocculation as previously described. The solid 106 is drawn out as a thickened slurry to be returned to
15 tank 100 or, if the magnesia is fully loaded, to dewatering as previously described.

In a further embodiment advantage is taken of the propensity of the bed volume to increase as it becomes laden with phosphorous. Thus the orthophosphate
20 containing influent - previously supplemented with calcium and/or decarbonated if required - is introduced into the bottom end, which is preferably cone shaped to facilitate uniform liquid distribution, of a cylindrical reactor previously charged with magnesium oxide. As the process
25 proceeds, the reaction mixture becomes increasingly enriched in deposited phosphorous, and as a consequence of this and the upflow velocity within the reactor, the overall bed volume increases. The bed volume increasingly occupies more of the total reactor volume and the "line of
30 demarcation" between the reactive mass and the clear supernatant, now substantially depleted in orthophosphate, steadily rises up the cylinder.

In this operational mode the bed is allowed to rise to a particular height in the reactor, and the phosphorous
35 enriched slurry withdrawn through an appropriately sized

port either continuously or in aliquots drawn off at set time periods. Since the bed volume rises at a much slower rate than the rate of influent flow through the reactor, the volume of the withdrawn slurry typically amounts to only 3-5% of the overall flow and the major portion of the effluent leaves the reactor via a port situated higher up the reaction vessel. Of course, it is necessary to replace the "lost" bed volume with fresh magnesium oxide, and this operation can be performed in either a continuous or semi-continuous manner.

By judicious selection of the initial mass of MgO , and depending on the influent flow rate and orthophosphate concentration, it is possible to design the reactor in such a manner that the solid content of the drawn off slurry has any desired phosphorous concentration.

In this mode of operation there is no necessity to recycle the slurry, although the slurry must be dewatered with the supernatant returned to the major effluent stream.

This embodiment is illustrated schemically in Fig. 4, with features like those of the embodiments of Figs. 1 and 2 and like numbered. Specifically, in this case as the bed volume of loaded magnesia rises, effluent 38 leaves the vessel 22 via a port 201 at an upper end thereof. Fresh magnesia 202 is added back to maintain the bed volume in the vessel 22.

Regardless of the configuration employed and depending upon the liquid throughput and settling properties of the reaction mass, if fine particle carryover is excessive this may be addressed through a final filtration step possibly assisted by polymer assisted flocculation.

In the latter case it has been found deleterious to the process to recycle the small amount of floc produced back to the main reaction vessels, since the residual polymer appears to impair the activity of the magnesium

- 16 -

oxide.

In all cases the process in the reactor operated at a high pH whereby magnesium oxide is contacted with the phosphorous containing stream should be of from about 8
5 to 12. Preferably the pH will be from about 9 to about 11. The selection of pH is dictated by the solubility of magnesium hydroxide. If required, the pH of the effluent may be reduced by dosing dilute mineral acid - eg, sulphuric acid - or by final treatment with carbon
10 dioxide - ie, recarbonation.

From the description given, it will be apparent that the present process represents a fundamentally different approach to those described in the prior art, and specifically, the present invention relies on the use of
15 fine grained magnesia and on a reaction vessel in which the magnesia is present as an agitated rather than a fixed bed.

The processes of both Kaneko et al and of Hirasawa et al employ granular medium in fixed beds, whilst Roques
20 et al use a half burnt dolomite material which is chemically different to the magnesia of the present invention.

Furthermore, it is to be noted that Roques et al teach their half burnt dolomite be added as a finishing
25 step to biological treatment of sewage. At that stage there will be a substantial amount of organic material present in addition to the dissolved phosphorous. This organic material will be adsorbed onto their medium thereby occluding the active surface area and consequently
30 impairing its ability to fix large quantities of phosphorous. This fact is recognised by the authors when they refer to the half burnt dolomite as an aid to settling of the biological floc.

Essentially their process is one describing a method
35 to enhance the settling characteristics of treated sewage,

- 17 -

which also may remove some of the phosphorous.

In order to better understand the nature and scope of the scope of the present invention, some laboratory scale experiments which embody different reactor configurations and methods of operating the process will be described. These experiments were performed on both the bench scale and on a small pilot rig capable of handling stream flows of 50 litres per hour.

Examples of the Process

10 Example 1

This laboratory bench scale experiment followed the flow diagram of Fig. 1 using the apparatus shown in Fig. 5. This was an initial experiment and served to define and develop the general operating conditions for the process which were incorporated into the conduct of subsequent experiments.

The apparatus used for this experiment will now be described with reference to Fig. 5.

An influent 320, previously decarbonated and containing phosphorous and supplemented with calcium ions, was pumped into the bottom 323 of a 2.5L conical reactor using a peristaltic pump (not shown). The reactor had been previously charged with magnesium oxide to form a bed 324 to a height 326. A glass wool plug 321 in the bottom 323 of the reactor 322 was used to retain the bed 324 in the reactor and to prevent it flowing back into the feedline.

A stirrer 325 was used to agitate the contents of the reactor 322. After a time, the level of the contents of the reactor rose to a height 327. At this point, effluent was allowed to drain by gravity 328 through a perspex tube 329 containing a wad of glass wool 339.

After filtration, the phosphorous depleted stream 331 flowed into a 3L receiving vessel 332. Effluent filtered and depleted in phosphorous was then removed 340 from the

- 18 -

vessel 332.

The first experiment using this apparatus will now be described in detail as follows:

Tertiary effluent from Quakers Hill sewage treatment
5 plant (near Sydney, Australia) was enriched in phosphorous
from the ambient 1-2mg/L using disodium hydrogen
phosphorous, so as to give the reactor an influent
phosphorous concentration of between 10 and 40 mg/L. The
calcium level was also supplemented using CaCl_2 with
10 typically the calcium ion concentration between 70 and
140mg/L.

Bicarbonate and dissolved carbon dioxide which could
interfere with phosphorous deposition by competing for
available calcium and depositing calcite (CaCO_3) in the
15 reactor was present in the sewage at around 120mg/L HCO_3
and was removed by air stripping. The pH was lowered from
around 7 to 4-4.5 using dilute sulphuric acid and then air
bubbles - from a fish tank aerator - were blown through
the liquid for around one half hour. The pH was then
20 adjusted back to 6.5-7.5 using dilute sodium hydroxide
solution. However other alkaline materials such as lime
or ammonia solutions could have been employed. Note that
the subsequent exposure to the MgO bed would have
neutralised the residual acid. However, this may also
25 have led to some redissolution of previously deposited
phosphorous, and possibly lead to difficulties in
interpreting the reactor and process performance.

The liquid 320 was then pumped to the bottom 323 of
the conical reactor 322 using a peristaltic pump at a flow
30 rate of between 500 and 1000mL/H. The reactor employed
had a conical bottom section of volume 1.5 litres and a
cylindrical top section of volume 1 litre giving total
reactor volume of 2.5 litres. At the start of the
experiment the reactor was charged with 100gm of fine
35 particulate magnesium oxide 324 - commercially available

- 19 -

as Enviromag-75 (ICI) and a small plug of fine glass wool 321 was fitted into the bottom of the conical section to prevent the solid reactor contents flowing back into the feed line.

5 The reactor was also fitted with a stirrer 325 designed so as to gently agitate the reactor contents. This was found necessary to prevent channel formation in the bed which "short circuited" the system and significantly reduced the performance of the process. The
10 stirring speed was about 40rpm.

 In operation the apparent volume of this reactive bed expanded by a factor of around 4 as a consequence of the upward fluid flow and gentle stirring. As time went on and the phosphorous content of the bed increased, so the
15 total bed volume also gradually increased.

 At height 327 effluent from the reactor 322 was allowed to overflow 328 into a downflow gravity filter simply made from a perspex tube 329 (30mm diameter) fitted with a wad of glass wool 339, and then into a receiving
20 vessel 332 of 3 litres capacity. This filter simply retained any particles carried over from the reactor and prevented them being carried with the final effluent 380. It was found that this device was required only for the first 200 hours of operation, since after this time the
25 settling characteristics of the particles in the reaction bed had improved, presumably as a consequence of now being coated with calcium phosphate and providing the reactor operation was not disturbed by violent agitation little or no solid material overflowed from the reactor vessel.

30 The experiment was run for 1500 hours with influent P levels between 2mg/L (unsupplemented sewage from the sewage treatment plant) and 45mg/litre. The system was operated at ambient temperature, ie 20-25 degrees C.

 Effluent samples were regularly taken from the
35 receiving vessel and analysed for orthophosphate using the

- 20 -

molybdenum blue method described in standard 4500-P of the 1992 edition of the American Water Works Association publication "Standard Methods for Examination of Water and Wastewater".

5 The level of total effluent orthophosphate (that contained within fine particles which were carried over from the reactor plus the truly soluble "ionic" phosphorous) were determined, as well as the level of the truly soluble component, determined after filtration of
10 the effluent through a 0.45 micron filter.

 The course of the reactor performance is summarised in the plots in Fig. 7, and an appreciation of the degree to which fine particulate matter was carried over can be gained from comparing the plots of orthophosphate in the
15 filtered and unfiltered effluent. Note that in order to clarify the levels of filtered and unfiltered phosphorous, the unfiltered levels have been multiplied by a factor of 2. The percentage of phosphorous removed was calculated on the phosphorous content in the filtered effluent.

20 Provided gentle stirring was maintained and adequate calcium was available for phosphorous deposition, the system - as operated in this laboratory study - consistently removed more than 95% of the influent orthophosphate, even from streams containing
25 >40mg/L P.

 On completion of the experiment, the solid contents were removed from the reactor, dried to constant weight at 105 deg C and analysed. The final dry weight was 160 grams assaying at 27% PO_4 (ie 9% P), 14% Ca and
30 50% (unused) magnesium hydroxide.

Example 2

 Tertiary treated sewage from Penrith sewage treatment plant - near Sydney, Australia - containing around 4mg/L phosphorous (as orthophosphate) was supplemented with
35 additional disodium hydrogen orthophosphate so that it

- 21 -

contained around 20mg/L elemental phosphorous. Calcium chloride or calcium sulphate (gypsum) was also added so that the sewage contained 110-140mg/L calcium. This sewage also contained around 120mg/L of HCO_3 , and in
5 this experiment no decarbonation of the influent to the MgO reactor was performed in order to ascertain any detrimental effect of this component on the process.

The influent, so prepared, was pumped to the reactor - again charged with 100gm of the MgO, and the experiment
10 conducted over a period of 1034 hours using the same apparatus, and in the manner described in Example 1.

Surprisingly, it was found that the presence of carbonate in the influent had no detrimental effect on the efficiency of the process to remove phosphorous, with
15 >99% of the influent soluble orthophosphate being deposited on the MgO bed. Titrations of influent and effluent indicated that only around 20% of the bicarbonate present in the feed stream was deposited as calcite within the reactor. The effluent was, however, supersaturated in
20 CaCO_3 and some calcite scale formed in the receiving vessel.

In this respect, however, it was found that unless gentle stirring was maintained, then some calcite was deposited at the bottom of the reactor, particularly in
25 the glass wool plug, which both impaired the flow rate into the reactor and contributed to channel formation in the main body of the MgO bed.

The course of the experiment is plotted in Fig. 8.

On completion of this trial, the dry weight of the
30 reactor solids was 182gm assaying at 26.7% PO_4 (ie, 8.9% P), 15.2% and 49% magnesium hydroxide.

Examples 1 and 2 demonstrated the applicability of the process for the removal of orthophosphate from tertiary treated sewage. Other analyses conducted on the
35 influent and effluent from these two experiments indicated

- 22 -

that some fluoride and silica - constituents of sewage - were also removed. Thus, in Example 2, fluoride was reduced from 1.0mg/L in the influent to 0.7mg/L in the effluent, while silica was reduced from 3.5 to 2.5mg/L.

5 It is also important to note that no biological growth was noted in the reaction bed despite the fact that the influent originated from sewage.

Example 3

This experiment was conducted using the same
10 equipment as in the previous tests, but employed secondary treated sewage from Round Corner sewage treatment plant near Sydney, Australia. This is a small plant employing only secondary biological activated sludge treatment and consequently the influent to the MgO reactor contained a
15 higher loading of organic matter and suspended solids than in the previous tests. This influent also contained ambient phosphorous levels of around 8mg/L total phosphorous, including 7mg/L of phosphorous as orthophosphate since no specific phosphorous removal is
20 undertaken at this plant.

No decarbonation was performed for this test, and influent preparation consisted only of supplementing calcium to around 80mg/L using calcium chloride.

In this trial, the reactor was charged with 50gm of
25 MgO and the influent again pumped at between 500 and 1000mL/hour. The test was run over 142 hours and soluble orthophosphate was removed to better than 95%. In this test, however, a good deal of fine particulate material carried over from the reactor, and up to 70mg/L of
30 suspended solids were recorded in the reactor effluent. Up to 20% of the deposited phosphorous was associated with this fine material. When, however, the effluent was treated with a little anionic polymer to flocculate and settle this material, in this cases 2-3mg/L of Alfloc 627
35 (provided by Nalco Aust.) at the ambient effluent pH of

10.2-10.5, the phosphorous as orthophosphate levels (unfiltered) fell to 0.2-0.3mg/L.

It was unclear whether the high particulate carryover observed during this experiment was due to the composition or nature of the secondary treated sewage, or to over-enthusiastic stirring during the course of the experiment.

In any case, this trial showed that the orthophosphate could be effectively deposited as calcium phosphate from secondary treated sewage, and also that excessive particulate carryover could be controlled by use of anionic floc promoting polymers.

The residual reactor solids from this experiment weighed 67gm and contained 2.2% P (6.6% PO_4). As with the two previous examples, despite the sewage origin of the influent, no biological growth was noticed on the bed.

Example 4

This experiment was run using a mixed bed of MgO and gypsum in order to explore the feasibility of negating the calcium preconditioning step, by including this process within the main reactor. The process steps are those shown in the Fig. 2 flow diagram.

The experiment was conducted using the same equipment as for Examples 1-3. However, an artificial influent was made up containing only orthophosphate at a concentration of 35-40mg/L and at a pH of 6.5-7.

The influent contained no calcium apart from that present in the make up water which was around 5-10mg/L. Again, this was pumped into the reactor at a flow rate of 500-1000mL/hour. The reactor was initially charged with 100gm of gypsum ($\text{Ca}(\text{SO}_4 \cdot 2\text{H}_2\text{O})$) over which was added a layer of 100gm of fine magnesium oxide. As the influent percolated through the gypsum bed, it became enriched in Ca ions, which thus enabled the deposition of calcium phosphate when the liquor encountered the overlaying, high

- 24 -

pH environment provided by the magnesium oxide bed.

During the course of this experiment, it was found that the relatively dense gypsum (SG - 2.30) always remained below the magnesium oxide/calcium phosphate layer whose SG appeared to be significantly lower, presumably because of the very low density of the amorphous calcium phosphate deposit.

Because of the relatively high solubility of calcium sulphate (about 2gm/L in saturated solution at 25 deg C), it was found necessary to replenish the gypsum bed from time to time, and over the course of the run 140gm of gypsum - additional to that present in the reactor at the start of the run - was added.

The experiment was run for 514 hours over which time 17.1gm of elemental P was deposited on the bed. The final dry weight of the reactor solids was 260gm, which assayed at 19.5% PO_4 (6.5% P), 20% Ca, 47% $\text{Mg}(\text{OH})_2$ and an estimated 21% of undissolved calcium sulphate.

The course of this run is illustrated in Fig. 9.

20 Example 5

This experiment was conducted with a high orthophosphate influent, ie, 20-60mg/L, supplemented appropriately with calcium, ie, 120-230mg/L, in order to ascertain the level to which the final reactor solids could be enriched in elemental phosphorous, consistent with a high percentage of phosphorous removal from the influent stream.

The reactor was the same as that used in the previously described Examples, and again the influent flow rate was 500-1000mL/hour. The trial was conducted over 1218 hours during which time 39.4gm of elemental P (present in the solution as orthophosphate) was passed through the reactor, and 37.7gm of elemental P was deposited on the bed. This represented 95.6% recovery of phosphorous.

- 25 -

Final solids recovered from the reactor at the conclusion of this experiment weighed 205gm dry, and contained 45% PO_4 (18% P), 29.7% Ca and only around 16% magnesium hydroxide. This product represents a high grade phosphorous raw material.

In the following three Examples, a much larger scale apparatus was used in order to ascertain the efficiency of the process at larger scale, and also to investigate the previously noted growth characteristics of the bed as the phosphorous loading increased.

The reactor 422 employed has a cone shaped bottom 423 as before, but had a significantly larger volume at 30 litres. The reactor dimensions are illustrated in Fig. 6. Influent 420 was pumped into the cone portion at a flow rate of 25-28 L/H, and this corresponded to a reactor surface loading of 1m/H. Magnesium oxide had been previously charged to the reactor to give a bed 424 to a depth 426. This was retained in the reactor by a non-return leaf spring 429. Influent 420 was controlled by manifold 421. In these experiments, the reactor effluent was gravity fed 428 to a 5 litre settler 434 into which anionic polymer 431 (Alfloc 627) was fed at a rate giving 2-3mg/L polymer in the effluent. This treatment successfully flocculated the small amount of particulate matter 433 carried over in the reactor effluent. A stirrer 430 was used to agitate this tank. Once deflocculated, the phosphorous depleted contents 432 were removed via line 436.

Example 6

This example followed the flowsheet of Fig. 1, using an artificial influent containing 15mg/L phosphorous and supplemented in Ca to 110mg/L. The reactor was charged with 50 grams of magnesium oxide and influent pumped into the system at 25L/H over a period of 30 hours.

In this experiment, the soluble phosphorous content

- 26 -

of the 0.45 micron filtered effluent never exceeded 0.2mg/L, while the phosphorous content from the unfiltered flocculated effluent from the settler was typically 0.2-0.5mg/L. The retention time in the settler was very short at about 12 min and longer settling times would probably have improved the quality of this effluent.

During the course of this experiment, the volume of the bed in the reactor was observed to increase until approximately 7 grams of phosphorous had been deposited, after which time it remained reasonably constant.

On completion of the run, the dried solids from the reactor weighed .86 grams and assayed at 11.7 P (35% PO_4) and 25.6% Ca.

The dry flocculated material collected from the settler weighed 3.3grams.

Example 7

This experiment was conducted in an identical manner to Example 6 except that the influent also contained 120mg/L of bicarbonate in addition to the 15mg/L phosphorous (45mg/L of PO_4).

As for Example 2, it was found that the presence of carbonate in the influent had no deleterious effect on the phosphorous removal, with soluble phosphorous in the reactor effluent never exceeding 0.26mg/L. The presence of carbonate did, however, have a dramatic impact on the volume of the reaction bed, leading to significantly smaller bed volumes than was the case when carbonate was absent from the influent. This effect is illustrated in Fig. 10 in which the bed volumes for both Examples 6 and 7 are plotted against the progress of the two experiments.

The effect of carbonate on decreasing the reactor bed volumes has been noted in other experiments not described here, and would appear to be of some importance when considering the engineering aspects of scaling up the process.

- 27 -

The final reactor solids (dry weight 107gm) assayed at 9.5% P and 28.1% Ca. The increased ratio of Ca/P recorded in this experiment is due to a relatively small amount of CaCO_3 co-deposited with the calcium
5 phosphorous. In this experiment, 7.1grams of dry flocculated material was recovered from the settler.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments
10 without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

- 28 -

CLAIMS

1. A process for the removal of phosphorous, in the form of orthophosphate, from an aqueous system, comprising introducing into the stream an effective amount of calcium
5 ions, optionally decarbonating the stream prior to the introduction of the calcium, adjusting the pH to between about 5 and 8, introducing the stream into a reaction vessel, contacting the stream with an amount of magnesium oxide in the form of fine particles sufficient to fix the
10 so-formed calcium phosphate, the pH of the stream in contact with the magnesium oxide being from about 8 to 12, whilst agitating the magnesium oxide and removing a stream from the vessel which is depleted in phosphorous.
2. A process as in claim 1, wherein the stream is
15 introduced into the reaction vessel in a manner such that it flows upwardly.
3. A process as in claim 1 or claim 2, wherein calcium is provided to the stream by a bed of gypsum disposed in a lower portion of the reaction vessel.
- 20 4. A process as in claim 1, wherein the calcium-containing liquid stream is introduced into a reaction vessel containing a continuously stirred slurry of magnesia which, when appropriately loaded with phosphorous, is allowed to overflow into a settling or
25 thickening apparatus, to form a thickened phosphorous laden slurry which is returned to the reaction vessel, and a phosphorous depleted liquid stream.
5. A process as in any one of claims 1 to 4, wherein the calcium is in the form of a soluble salt, preferably
30 gypsum or calcium chloride.
6. A process as in any one of claims 1 to 5, wherein the calcium ions are introduced into the stream by diverting a portion thereof to a tank, adding the calcium to the stream contained therein and returning the calcium-dosed stream
35 to the stream to be introduced into the reaction vessel.

- 29 -

7. A process as in any one of claims 1 to 6, wherein the liquid stream is decarbonated prior to the introduction of calcium ions.
8. A process as in claim 7, wherein decarbonation is
5 achieved by adding sufficient acid to the liquid stream contained in a vessel so as to lower the pH to about 4-4.5 and air stripping the stream.
9. A process as in claim 8, wherein alkali is added to the decarbonated stream to give a pH of about 5-8.
- 10 10. A process as in any one of claims 1 to 9, wherein the contents of the reaction vessel are agitated in a manner to just prevent the formation of channels in the bed of magnesium oxide.
11. A process as in any one of claims 1 to 10, wherein
15 the magnesium oxide has a particle size of less than about 200 microns.
12. A process as in claim 11, wherein the magnesium oxide has a particle size of less than about 100 micron.
13. A process as in claim 12, wherein the particle size
20 distribution of the magnesia is such that 95% by weight passes a 75 micron screen.
14. A process as in claim 13, wherein the magnesia has a mean particle diameter of about 10 micron.
15. A process as in any one of claims 1 to 14, wherein
25 the magnesium oxide is in the form of magnesia.
16. A process as in any one of claims 1 to 15, wherein the phosphorous depleted stream is subjected to filtration and flocculation.
17. A process as in claim 16, wherein flocculation is
30 achieved through the addition of an anionic polymer to the phosphorous depleted liquid stream.
18. A process as in any one of claims 1 to 17, wherein magnesium oxide or magnesia loaded with phosphorous is removed and dewatered with the liquid component being
35 returned to the reaction vessel and the solid component

- 30 -

removed for use as a fertiliser.

19. A process as in any one of claims 1 to 18, wherein the pH of the liquid stream prior to calcium addition is about 5-7.

5 20. A process as in any one of claims 1 to 19, wherein the pH of the contents of the reaction vessel is about 9-11.

21. A process as in claim 4, wherein the reaction vessel comprises an in-line mixer.

10 22. A process as in any one of claims 1 to 21, wherein the phosphorous containing aqueous stream is primary, secondary or tertiary sewage.

23. A process as in any one of claims 1 to 22, wherein the amount of calcium ions introduced to the liquid stream
15 to reduce phosphorous in the phosphorous depleted stream to $\langle 0.2\text{mg/L is sufficient to give a concentration } \rangle$ or $= [2 \times \text{Pin} + 80] \text{ mg/L}$ wherein Pin represents the concentration in mg/L of phosphorous in the liquid stream.

1/10

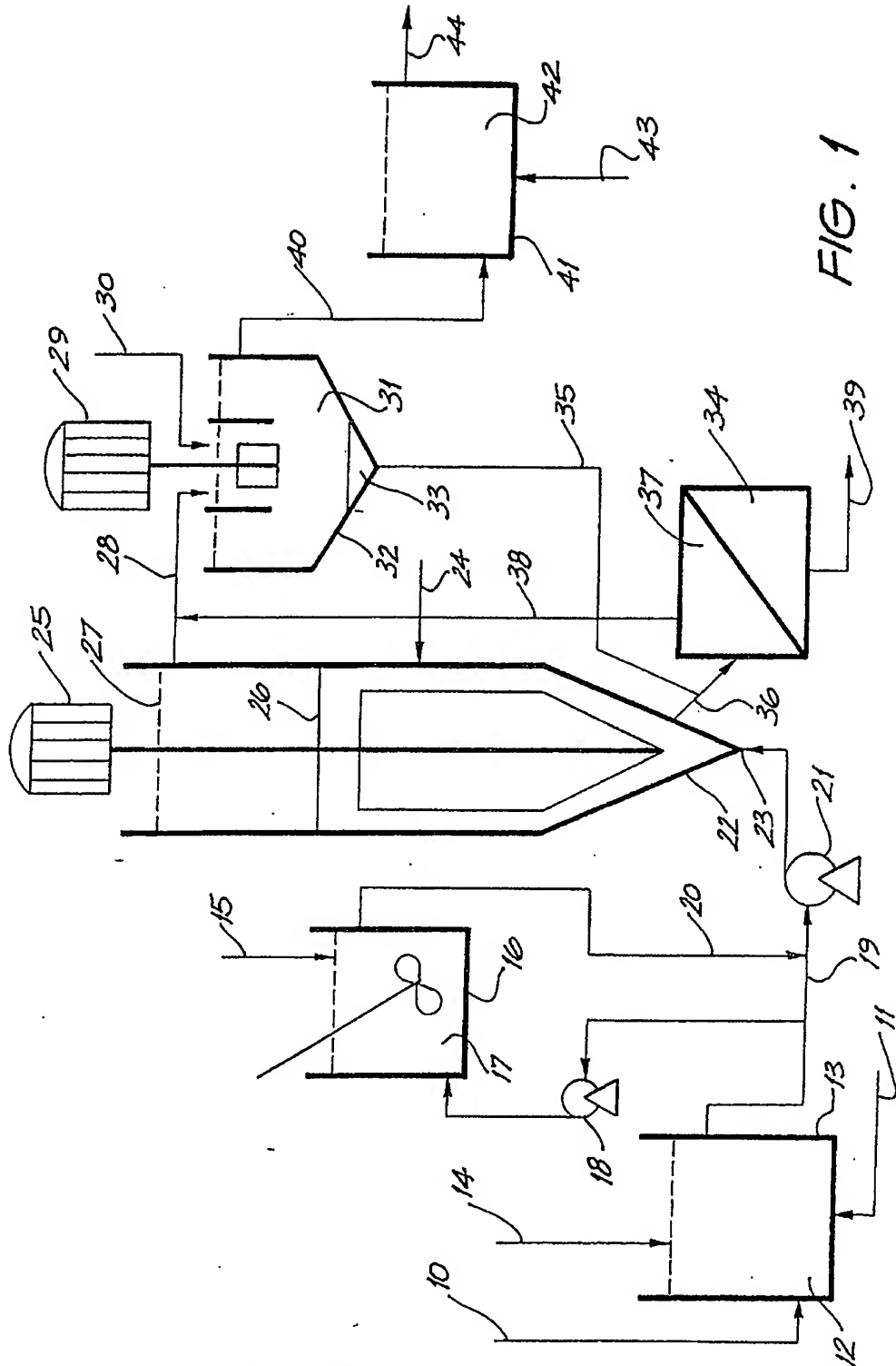


FIG. 1

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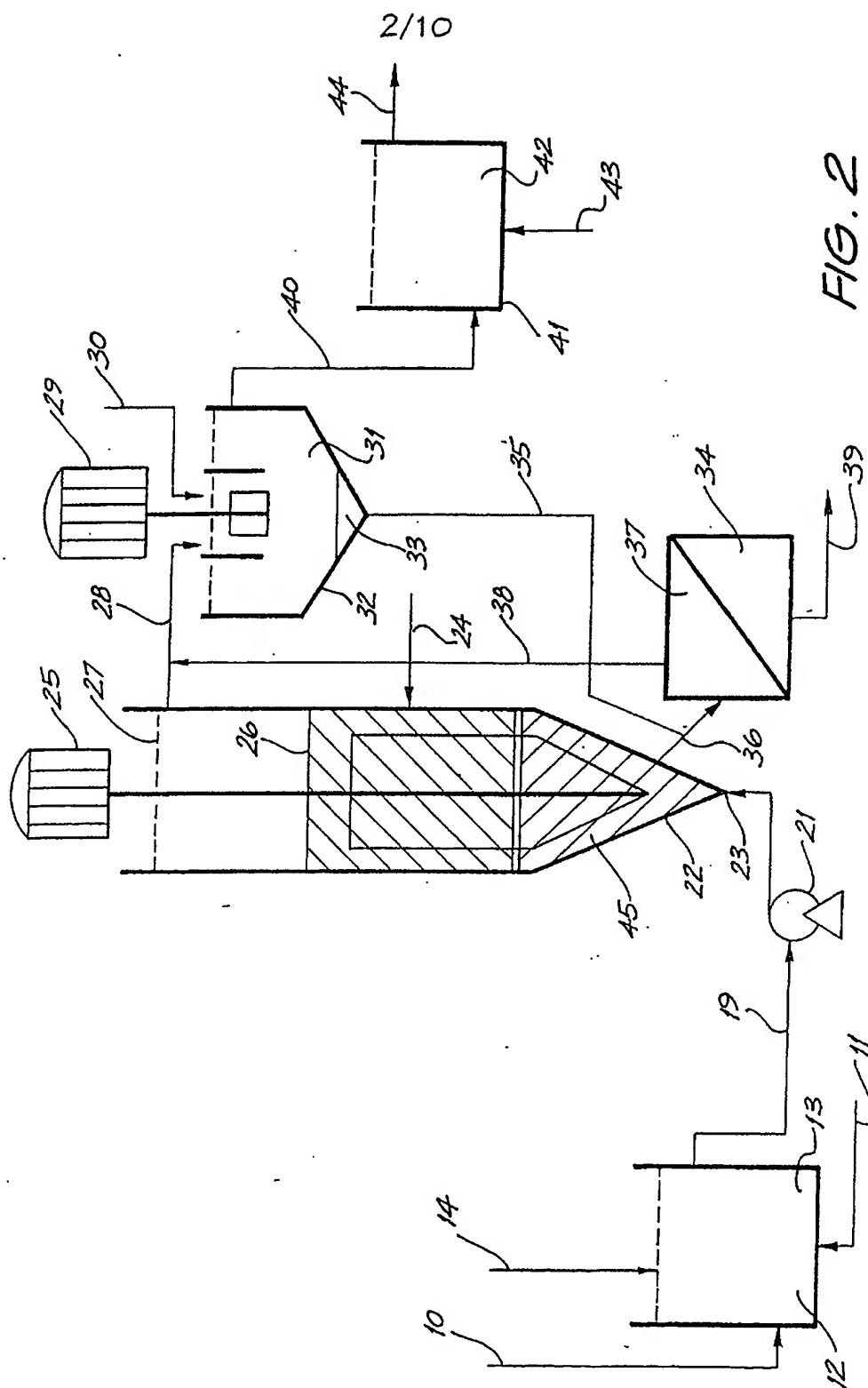


FIG. 2

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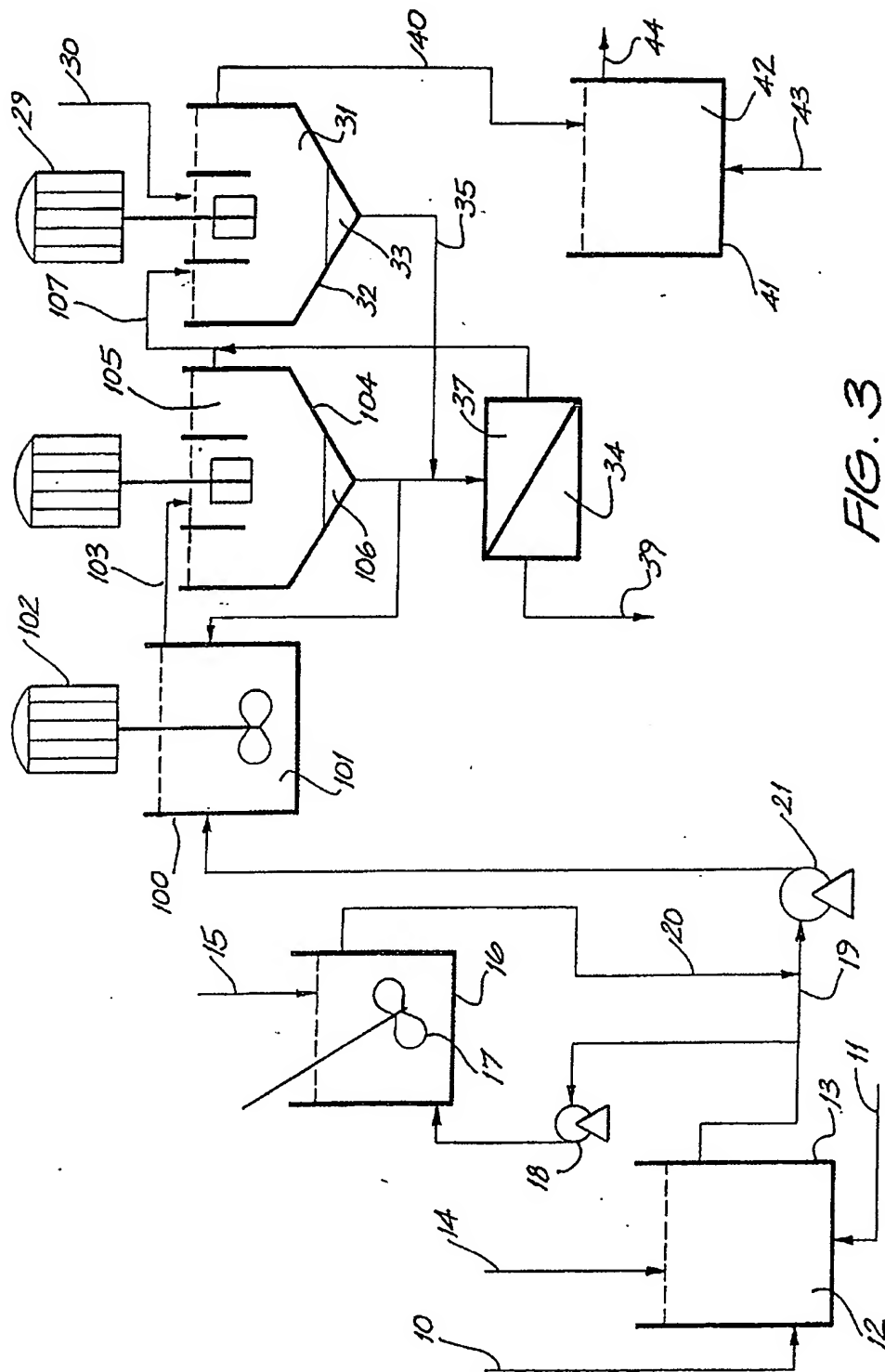


FIG. 3

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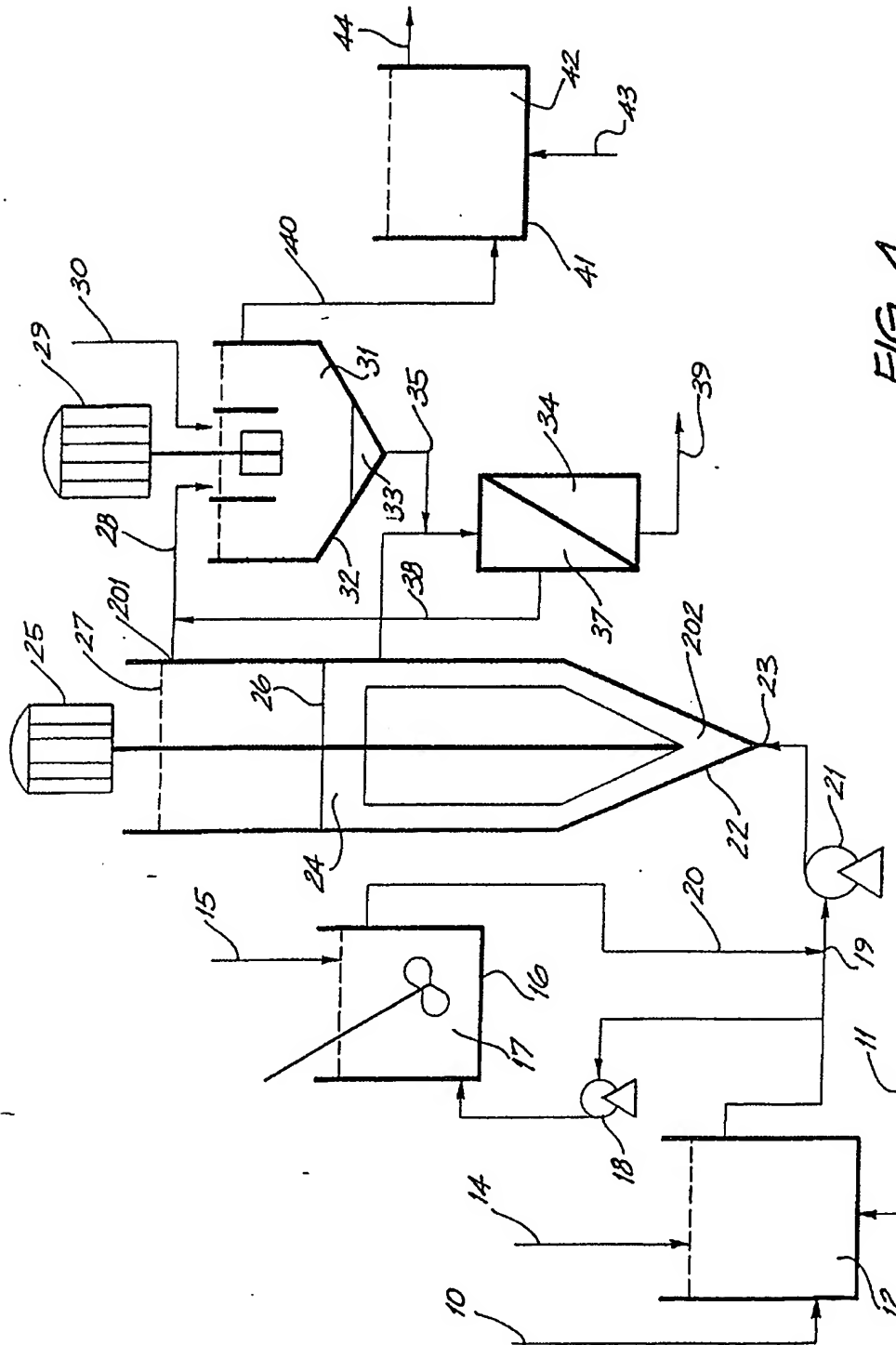


FIG. 4

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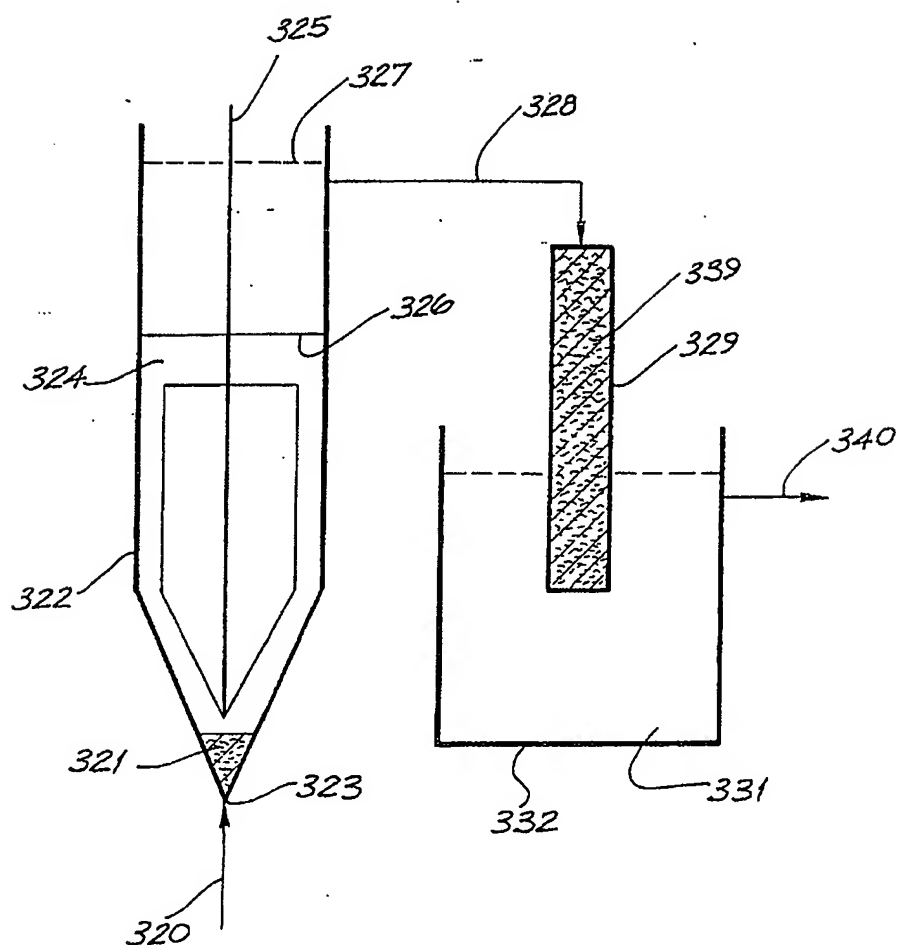


FIG. 5

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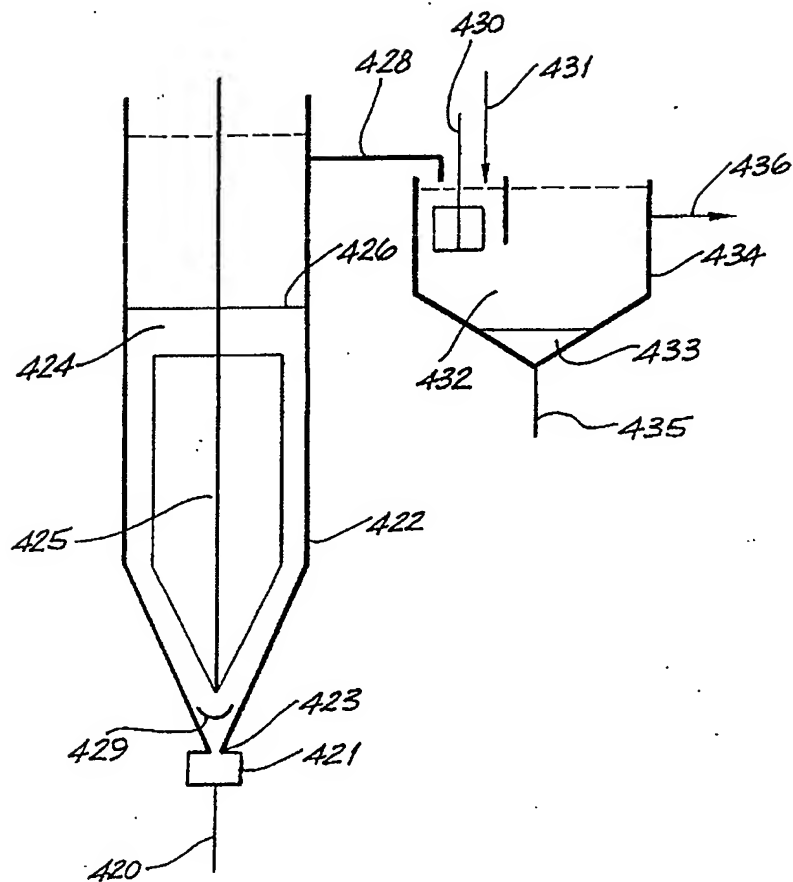
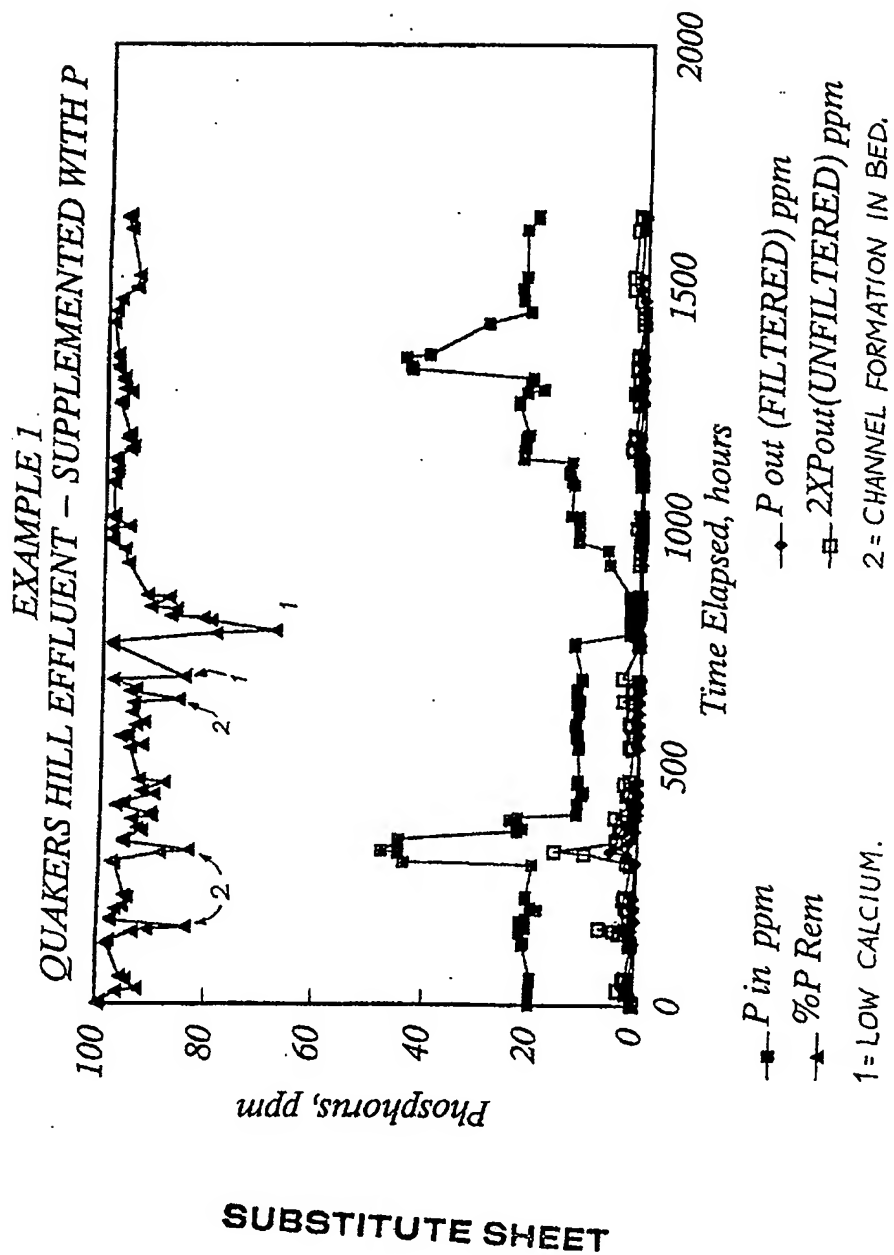


FIG. 6

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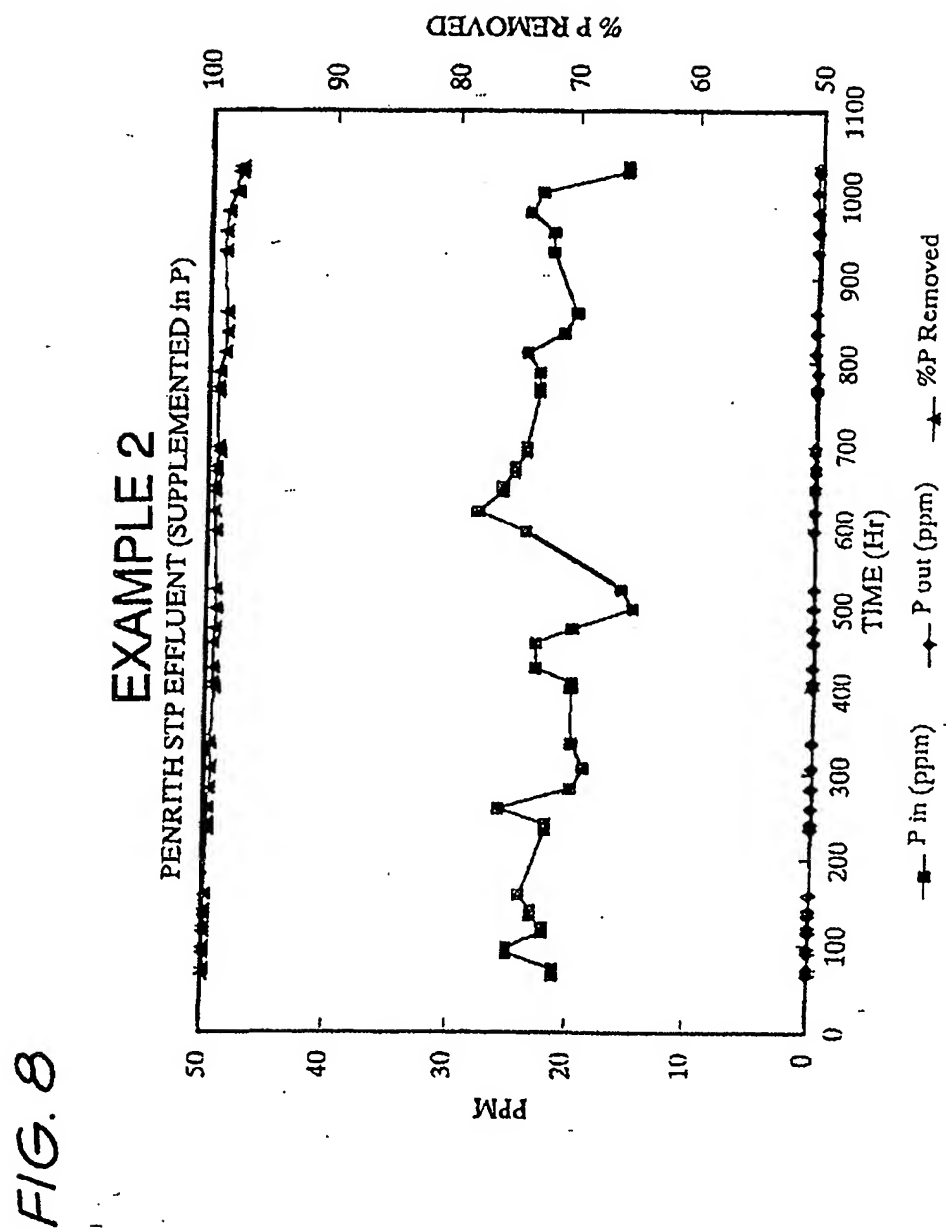
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FIG. 7



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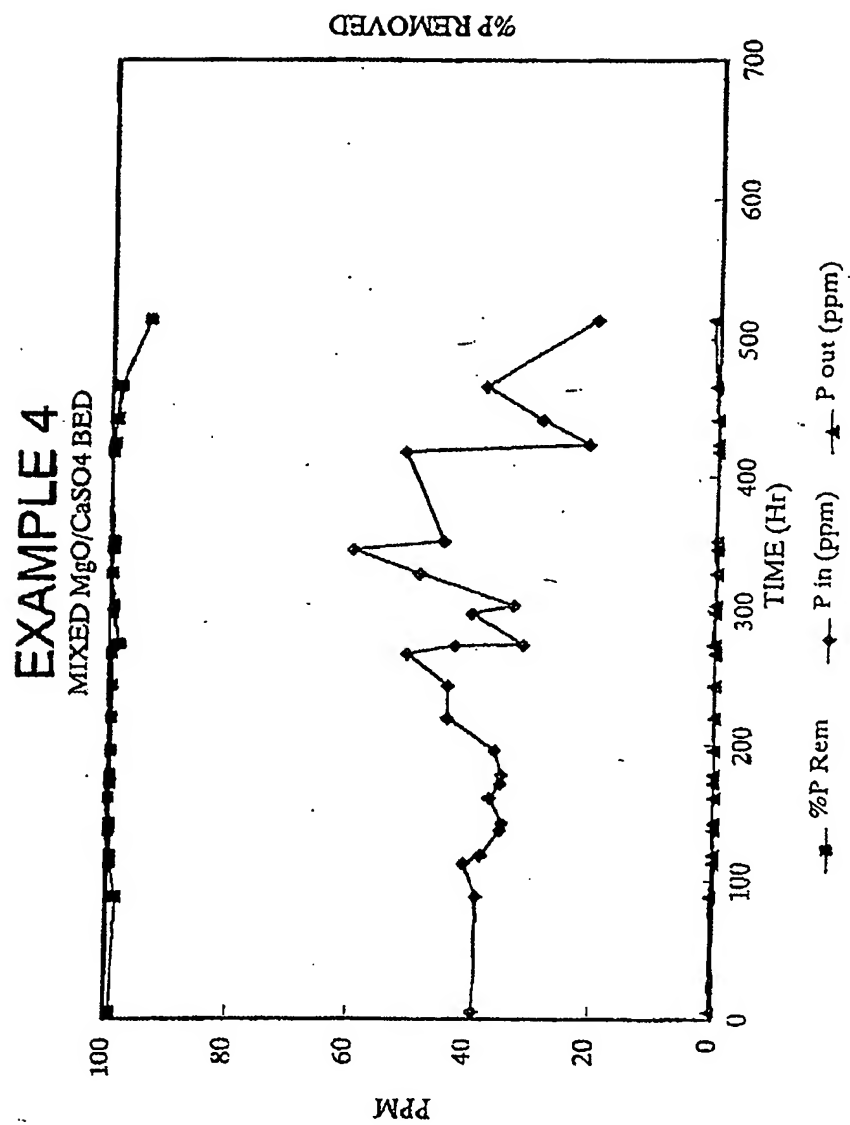
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FIG. 9



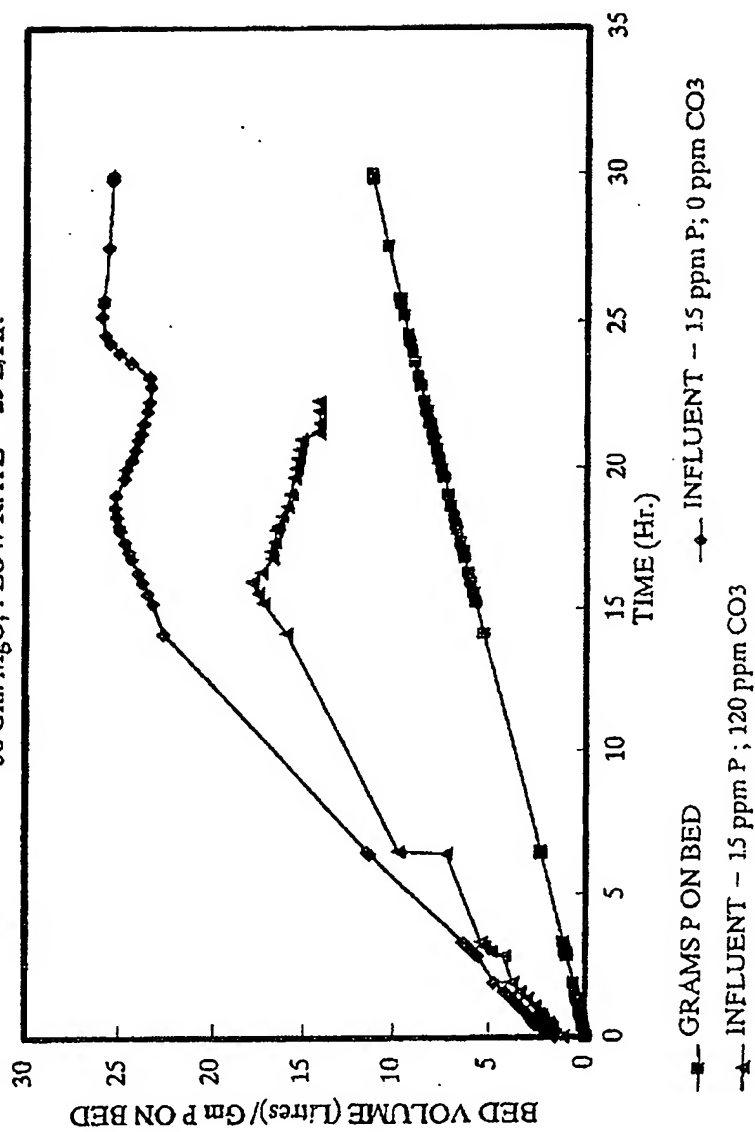
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FIG. 10

BED VOLUME - EXAMPLES 6&7


50 Gm. MgO; FLOW RATE = 25 L/Hr.



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 93/00303

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ C02F 1/58, 1/28 According to International Patent Classification (IPC) or to both national classification and IPC												
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC: C02F 1/58, 1/66, 1/68, 1/28, C02B 1/23, C02C 1/40, 5/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC C02F 1/58 Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT: IPC classes as above and C02B 1/14, 7/00 using keywords (phosph: or PO ₄) and (magnes: or Mgo) CHEMICAL ABSTRACTS: Keywords as above and (calcium or Ca or gypsum)												
C. DOCUMENTS CONSIDERED TO BE RELEVANT												
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.										
X	Derwent Abstract Accession No. 47250 E/23, class D15, JP,A,57-071693 (KATAYAMA KAGAKU KOG) 4 May 1982 (04.05.82) Abstract.	1-23										
X	Derwent Abstract Accession No. 84-223018/36, class D15, JP,A,59-132994 (KURITA WATER IND. KK.) 31 July 1984 (31.07.84) Abstract.	1-23										
X	Derwent Abstract Accession No. 84-259286/42, class D15, JP,A,59-156489 (KURITA WATER IND. KK.) 5 September 1984 (05.09.84) Abstract	1-23										
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.												
* Special categories of cited documents : <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier document but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed	
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"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone											
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art											
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family											
"P" document published prior to the international filing date but later than the priority date claimed												
Date of the actual completion of the international search 12 August 1993 (12.08.93)		Date of mailing of the international search report 3 SEP 1993 (3.09.93)										
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. (06) 2853929		Authorized officer  M. BREMERS Telephone No. (06) 2832052										

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 93/00303

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	Derwent Abstract Accession No. 85-306665/49, class D15, JP,A,60-212289 (KURITA WATER IND. KK.) 24 October 1985 (24.10.85) Abstract.	1-23
X	Derwent Abstract Accession No. 85-319722/51, class D15, JP,A,60-222189 (HITACHI PLANT ENG. CONST.) 6 November 1985 (06.11.85) Abstract.	1-23
X	Derwent Abstract Accession NO. 86-228353/35, class D15, JP,A,61-157391 (EBARA INFILCO KK.) 17 July 1986 (17.07.86) Abstract.	1-23
X	Derwent Abstract Accession NO. 86-295046/45, class D15, JP,A,61-216795 (EBARA INFILCO KK.) 26 September 1986 (26.09.86) Abstract.	1-23